

Directed motion and useful work from an isotropic nonequilibrium distribution

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We demonstrate that a gas of classical particles trapped in an external asymmetric potential undergoes a quasiperiodic motion, if the temperature of its initial velocity distribution T_{ne} differs from the equilibrium temperature, T_{eq} . The magnitude of the effect is determined by the value of $T_{ne} - T_{eq}$, and the direction of the motion is determined by the sign of this expression. The “loading” and “unloading” of the gas particles change directions of their motion, thereby creating a possibility of shuttle-like motion. The system works as a Carnot engine where the heat flow between kinetic and potential parts of the nonequilibrium distribution produces the useful work.

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Since the Maxwell demon thought experiment, the extraction of useful work and directed motion from unbiased nonequilibrium distributions has been the source of fascination, intrigue and confusion.¹ Being a fundamental scientific problem, it is also of significant practical interest for various biological and nanotechnological applications. Biological systems driven by the nonequilibrium fluctuations include translocases, which pull protein across membranes; kinesin, which walks along microtubules; myosin, which moves along actin in muscle; helicases, which unwinds DNA.² Recently, there have been a flurry of activities to harness nonequilibrium fluctuations to create various types of working nanodevices.^{3,4} In this Letter, we propose a new type of “motors” which are driven by the heat flow between nonequilibrium velocity and equilibrium coordinate distributions.

Consider a gas of classical non-interacting particles trapped in external potential $U(x)$. If the gas is in thermal equilibrium with a heat bath at the temperature T_{eq} , then positions (x) and velocities (v) of the gas particles have the equilibrium Boltzmann distribution:

$$\rho_B(x, v) = \rho_B(x)\rho_B(v); \quad (1)$$

$$\begin{aligned} \rho_B(x) &= \exp\{-U(x)\} / \int dx \exp\{-U(x)\}, \\ \rho_B(v) &= \sqrt{1/(2\pi)} \exp\{-v^2/2\}. \end{aligned} \quad (2)$$

We use the reduced variables in this Letter: Time, position, velocity, and energy are measured in units of $\sqrt{mL^2/(k_B T_{eq})}$, L , $\sqrt{k_B T_{eq}/m}$ and $k_B T_{eq}$, respectively (k_B is the Boltzmann constant, m is the mass of a gas particle and L is a unit of length).

Since equilibrium fluctuations cannot produce any directed motion, the average velocity of the gas $\langle v(t) \rangle_B = \int dv dx \rho_B(v, x) v(t)$ is identically zero at any time t . What happens if we instantaneously change the velocity distribution of the particles to some non-equilibrium distribution $\rho_{ne}(v)$? Apparently, if $\rho_{ne}(v) = \delta(v - v')$, then the gas undergoes a periodic motion within the potential well. Such a distribution (and akin non-singular distributions) are biased, since they predict nonzero mean initial velocity $\langle v(t=0) \rangle = v'$. In this Letter, we consider

more physically interesting and experimentally accessible situation, when the nonequilibrium distribution is unbiased and depends on the modulus of the particle velocity, $\rho_{ne}(|v|)$, so that $\langle v^{2n+1}(t=0) \rangle \equiv 0$ for any integer n . To be more specific, we assume for simplicity that $\rho_{ne}(|v|)$ can be represented by the Boltzmann distribution, but at a nonequilibrium temperature $T_{ne} \neq T_{eq}$:

$$\begin{aligned} \rho_{ne}(x, v) &= \rho_B(x)\rho_{ne}(v), \\ \rho_{ne}(v) &= \sqrt{\frac{1}{2\pi} \frac{T_{eq}}{T_{ne}}} \exp\left\{-\frac{v^2}{2} \frac{T_{eq}}{T_{ne}}\right\}. \end{aligned} \quad (3)$$

Such nonequilibrium distributions over molecular velocities and angular momenta are produced, for example, in the course of photodissociation $A + \hbar\nu \rightarrow B + \text{products}$,^{5,6,7,8,9} which is normally considered as instantaneous on the timescale of molecular translation and rotation.¹⁰ Indeed, let \mathbf{x}_i , \mathbf{p}_i , and m_i be the positions, the momenta, and the masses of the parent ($i = A$) and product ($i = B$) molecules. Since the parent molecule falls apart instantaneously, the positions do not change, $\mathbf{x}_B = \mathbf{x}_A$. As to the momenta, we can write⁹ $\mathbf{p}_B = (m_B/m_A)\mathbf{p}_A + \mathbf{\Delta}$. The first term here describes mapping of the parent molecule translation into that of the product. The quantity $\mathbf{\Delta}$ depends on the carrier frequency ν of the dissociating laser pulse and originates from the impulsive force arising due to the rupture of chemical bond(s) of the parent molecule. If the parent molecules possess initial equilibrium distribution over their positions and momenta, then dissociation preserves the original distribution over the positions, $\rho_B(\mathbf{x})$, but produces a nonequilibrium distribution over the momenta of photoproducts, $\rho_{ne}(\mathbf{p})$. If $\mathbf{\Delta} \neq 0$, then $\rho_{ne}(\mathbf{p})$ is a shifted Gaussian distribution. If the laser is tuned as to make $\mathbf{\Delta} = 0$, then $\rho_{ne}(\mathbf{p})$ is the Boltzmann distribution at the nonequilibrium temperature $T_{ne} = (m_B/m_A)T_{eq}$. In general, any reaction of the kind $A \rightarrow A'$ (photoassociation, photoisomerization) will create a nonequilibrium distribution over velocities of the species A and A' , provided the processes is rapid enough on the timescale of molecular dynamics.

We begin with the standard Newton equations of motion for non-interacting particles in potential $U(x)$:

$$v = \dot{x}, \quad \dot{v} = -dU(x)/dx. \quad (4)$$

In the equilibrium case, initial values of positions and velocities of the gas particles should be sampled from the Boltzmann distribution (1). Since our aim is to evaluate the average velocity,

$$\langle v(t) \rangle = \int dv dx \rho_{ne}(v, x) v(t), \quad (5)$$

we need to solve Eq. (4) with the initial nonequilibrium distribution (3).

This average velocity $\langle v(t) \rangle$ possesses several rather unusual properties. It is well known that any equilibrium correlation function calculated for any Hamiltonian system is an even function of time. This is a direct consequence of the time-inversion symmetry. In contrast, as is easy to demonstrate,

$$\langle v(t) \rangle = \sum_{n=0}^{\infty} G_n \frac{t^{2n+1}}{(2n+1)!} \quad (6)$$

is an odd function of time, so that $\langle v(t) \rangle = -\langle v(-t) \rangle$. This type of behavior is caused by the special initial nonequilibrium preparation of the gas at $t = 0$. We can calculate the first few terms in series (6) analytically:

$$G_0 = 0, \quad G_1 = \frac{T_{ne} - T_{eq}}{T_{eq}} \left\langle \frac{d^3 U(x)}{dx^3} \right\rangle. \quad (7)$$

As one may expect, G_1 is proportional to the difference between the equilibrium and nonequilibrium temperature, since all G_n must vanish at equilibrium. Eq. (7) shows that the external potential must not have a symmetry axis, in order to get $\langle v(t) \rangle \neq 0$.

To be more specific, we consider a gas trapped in the nonlinear asymmetric potential

$$U(x) = \omega^2 x^2 / 2 + a(x - s)^3 + b(x - s)^4. \quad (8)$$

Here ω is the harmonic oscillator frequency and the parameters a , b , and s describe the nonlinear part of the potential. One cannot analytically calculate $\langle v(t) \rangle$ for this potential. Therefore, we will compute it numerically but, first, it is instructive to show some results of the perturbation theory. Assuming that the anharmonic part of the potential is small and retaining linear in a and b contributions only, we get

$$\langle v(t) \rangle = -\frac{T_{ne} - T_{eq}}{T_{eq}} (3a - 12sb) \Phi(t), \quad (9)$$

where

$$\Phi(t) = \frac{2}{3\omega^3} \sin(\omega t) \{1 - \cos(\omega t)\}. \quad (10)$$

So, $\langle v(t) \rangle$ exhibits a periodic motion. Its magnitude and direction are determined by the value and sign of $T_{ne} - T_{eq}$. Since the difference in temperatures is readily linked to the difference of masses in distribution $\rho_{ne}(v)$, we see that “loading” and “unloading” of the particles

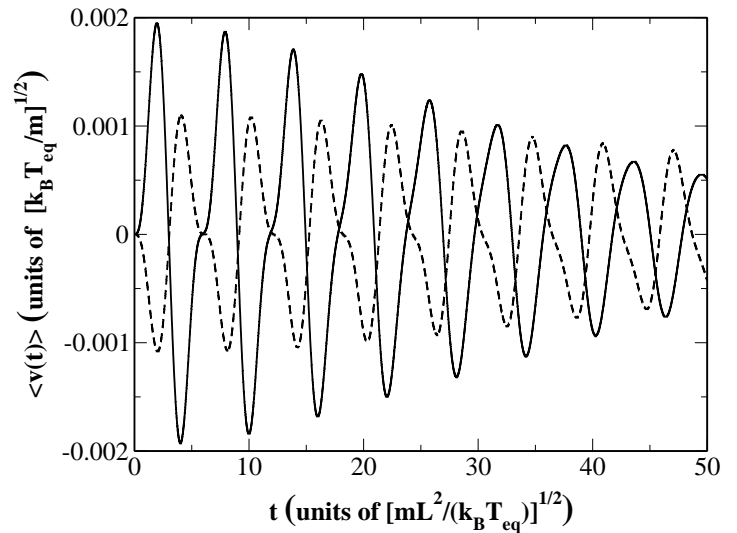


FIG. 1: Mean velocity $\langle v(t) \rangle$ for ideal gas of particles moving in the potential (8) with $\omega = 1$, $s = 0.2$, $a = 0.003$, and

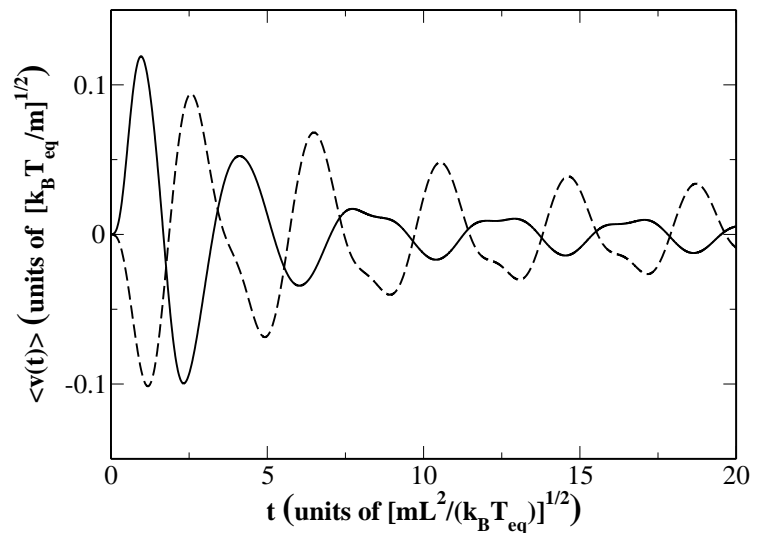


FIG. 2: Same as in Fig. 2 but for $s = 1$, $a = 0.3$, and $b = 0.5$.

(that is the increase and decrease of their masses) changes directions of their motion, thereby creating a possibility of shuttle-like motion.¹¹ Furthermore, if we consider dissociation $A \rightarrow B + C$, then (different) particles B and C are produced at different nonequilibrium temperatures and thus induce different fluxes, allowing for the mass separation.¹² The terms stemming from the cubic and quartic branches of $U(x)$ enter Eq. (9) with different signs and thus lead to the opposite senses of motion. Interestingly, the contributions cancel each other for $a = 4sb$, but this is valid only within the perturbation theory. Higher order terms ensure nonzero $\langle v(t) \rangle$.

We also compute $\langle v(t) \rangle$ exactly, solving numerically equations of motions (4) by Verlet algorithm for differ-

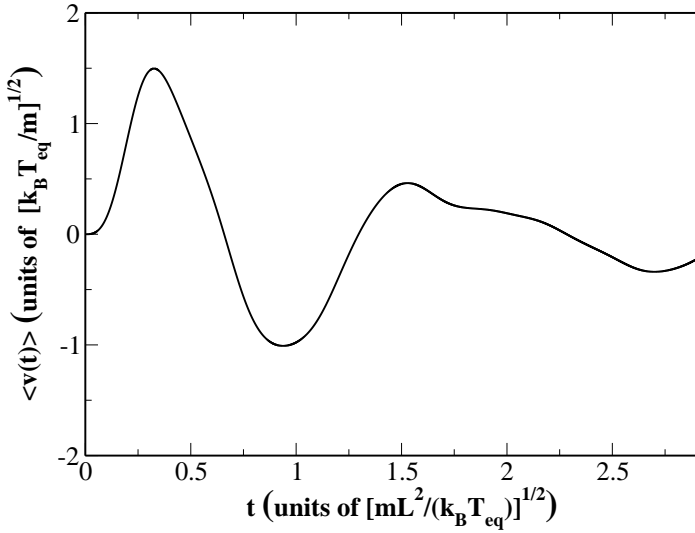


FIG. 3: Mean velocity $\langle v(t) \rangle$ for ideal gas of particles moving in the potential (8) with $\omega = 1$, $s = 5$, $a = 0$, and $b = 5$; $T_{ne} = 20T_{eq}$.

ent initial conditions sampled according to the nonequilibrium distribution (3). Typical behaviors of $\langle v(t) \rangle$ are presented in Figs. 1-3. If nonlinear corrections to $U(x)$ are small, then several first oscillations of $\langle v(t) \rangle$ in Fig. 1 are excellently described by the perturbative formulas (9) and (10). However, the oscillations decay in time, despite absence of dissipation. This can be understood by switching to the action (I) - angle (φ) variables. Then we can write

$$\langle v(t) \rangle = \sum_{n=1}^{\infty} \int dI d\varphi \rho_{ne}(I, \varphi) v_n(I) \exp\{in(\varphi - \omega(I)t)\}, \quad (11)$$

$v_n(I) \equiv (2\pi)^{-1} \int d\varphi v(I, \varphi) \exp\{in\varphi\}$ (evidently, $v_0(I) = 0$). As distinct from the harmonic oscillator, the frequency $\omega(I)$ of a nonlinear oscillator depends upon the action variable and $\langle v(t) \rangle$ decays due to dephasing.

If the the nonlinear contributions to $U(x)$ become more pronounced, then the magnitude of $\langle v(t) \rangle$ increases (Figs. 2 and 3), but the oscillations decay more rapidly. It is remarkable that $\langle v(t) \rangle$ can exceed the mean equilibrium thermal velocity $\sqrt{k_B T_{eq}/m}$ (Fig. 3). The corresponding value of the nonequilibrium temperature $T_{ne} = 20T_{eq}$ is not unreasonable, e.g., for hot *CN* fragments produced through photodissociation of *ICN* (see Ref.⁵).

The quantity $\left\langle \int_{x_1}^{x_2} F(x) dx \right\rangle = \langle v(t_2)^2 - v(t_1)^2 \rangle / 2$ can be regarded as the total ensemble-averaged work performed by the gas. Evidently, this quantity is identically zero at equilibrium. Under nonequilibrium conditions, this is nonzero oscillatory function (Fig. 4). The presence of oscillations means that, by choosing the appropriate time moments t_1 and t_2 , we can make the averaged work $\langle v(t_2)^2 - v(t_1)^2 \rangle / 2$ positive, irrespective of whether the nonequilibrium temperature T_{ne} is smaller or higher than the bath temperature T_{eq} . So, our system can be re-

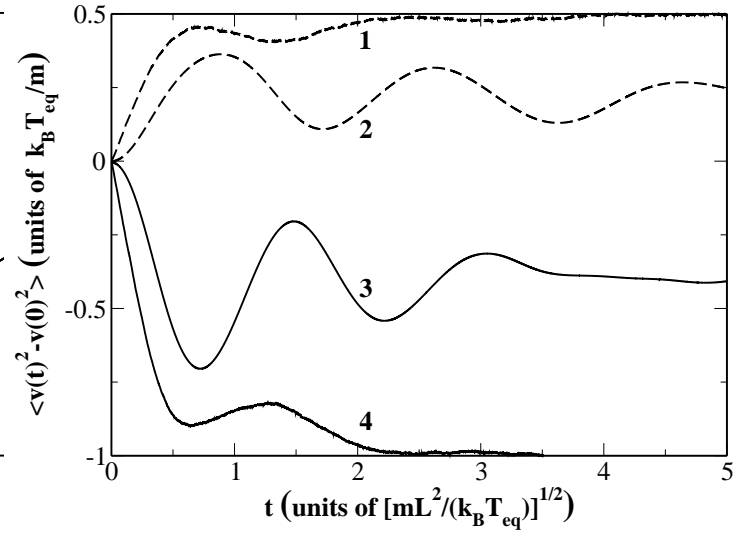


FIG. 4: Total ensemble-averaged work $\langle v(t)^2 - v(0)^2 \rangle$ for gas of particles moving in the potential (8) with $\omega = 1$, $s = 1$, $a = 0.3$, and $b = 0.5$; for $T_{ne} = 2T_{eq}$ (full line) and $T_{ne} = T_{eq}/2$ (dashed line).

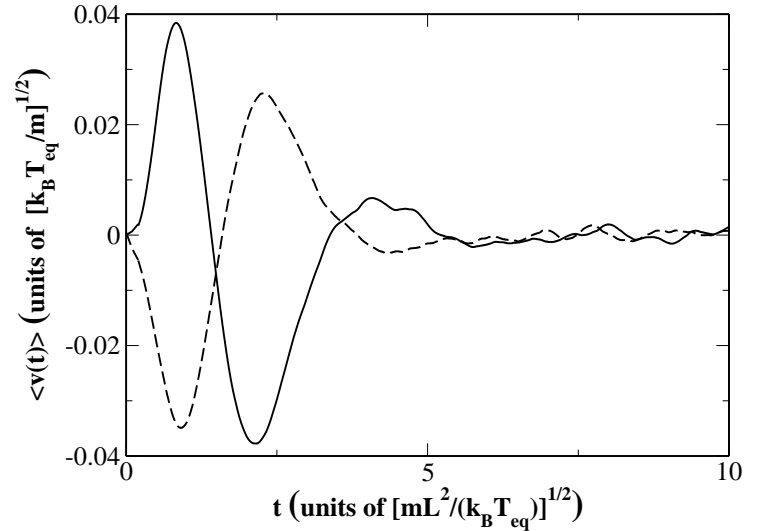


FIG. 5: Mean velocity $\langle v(t) \rangle$ for a moderately damped ($\xi = 1$) Brownian particle moving in the potential (8) with $\omega = 1$, $s = 1$, $a = 0.3$, and $b = 0.5$. Full line corresponds to $T_{ne} = 2T_{eq}$ and dashed line corresponds to $T_{ne} = T_{eq}/2$.

garded as a true heat engine, which produces a cycled motion out of unbiased nonequilibrium distributions and can be harnessed to make a useful work.

Now we turn our attention to the role of the system-bath interaction. We thus convert the Newton equation of motion (4) into the Langevin equation:

$$v = \dot{x}, \quad \dot{v} = -dU(x)/dx - \xi v + f(t). \quad (12)$$

Here, ξ is the friction and $f(t)$ is the stochastic white-noise force, which obeys the fluctuation-dissipation rela-

tion $\langle f(t)f(t') \rangle = 2\xi\delta(t-t')$. The coupling to the heat bath restores equilibrium distribution (1), so that eventually $\langle v(t) \rangle \rightarrow 0$ when $t \rightarrow \infty$. As in the bath-free case we can obtain the perturbative solution of Eq. (12), which is valid up to the terms linear in a and b . The result is again given by Eq. (9), in which one has to put

$$\Phi(t) = \frac{2}{\omega^2\sqrt{D}} \exp\left\{-\frac{\xi t}{2}\right\} \left[\frac{\xi + \sqrt{D}}{\xi - 3\sqrt{D}} \exp\left\{-\frac{\sqrt{D}}{2}t\right\} - \frac{\xi - \sqrt{D}}{\xi + 3\sqrt{D}} \exp\left\{\frac{\sqrt{D}}{2}t\right\} \right] - \frac{2}{D} \exp\{-\xi t\} \left[\frac{2}{\xi - 3\sqrt{D}} \times \exp\{\sqrt{D}t\} + \frac{2}{\xi + 3\sqrt{D}} \exp\{-\sqrt{D}t\} - \frac{\xi}{\omega^2} \right], \quad (13)$$

$D = \xi^2 - 4\omega^2$. In the underdamped case ($D < 0$), $\Phi(t)$ consists of two contributions, which oscillate at frequencies $\sqrt{-D}$ and $\sqrt{-D}/2$, and decay $\sim \exp\{-\xi t\}$ and $\sim \exp\{-\xi t/2\}$, correspondingly. Furthermore, there exists a monotonically decaying contribution $\sim \xi \exp\{-\xi t\}$, which is absent in the dissipation-free case. If $2\omega \gg \xi$, then Eq. (13) reduces to the damped analogue of Eq. (10)

$$\Phi(t) = \frac{2}{3\omega^3} \sin(\omega t) \exp\left\{-\frac{\xi}{2}t\right\} \left(1 - \exp\left\{-\frac{\xi}{2}t\right\} \cos(\omega t) \right). \quad (14)$$

We solve Langevin equation (12) numerically, as described in.¹³ Fig. 5 depicts $\langle v(t) \rangle$ calculated for moderate damping $\xi = 1$. A comparison of Figs. 2 and 5 reveals that damping, as expected, decreases the absolute value of $\langle v(t) \rangle$, but the effect definitely persists. The damping does not destroy the oscillation of the ensemble-averaged work shown in Fig.4. This means that the phenomenon of $\langle v(t) \rangle \neq 0$ is quite robust and may exist in dense gases and even liquids. In the overdamped case ($\xi \gg 2\omega$, $t \gg 1/\xi$) $\Phi(t)$ becomes $\sim \xi^{-3}$:

$$\Phi(t) = \frac{1}{\xi^3} \exp\left\{-\frac{\omega^2}{\xi}t\right\} \left(2 \exp\left\{-\frac{\omega^2}{\xi}t\right\} - 1 \right). \quad (15)$$

Note, however, that the question about the existence of $\langle v(t) \rangle \neq 0$ is not only about the strength of friction, but also about the corresponding timescale. Since motion of any Hamiltonian system is dissipation-free for $t \ll 1/\xi$, $\langle v(t) \rangle \neq 0$ on that time interval.

It has not escaped our notice that, with suitably selected external periodic potential, the system represents a new type of motor which convert the nonequilibrium disparity in the velocity and coordinate distribution into directed motion. Although both standard Brownian ratchets^{14,15,16} and our motor use the broken symmetry of the external potential and nonequilibrium fluctuations to produce the directed motion, there are three important differences between them. First, the standard Brownian motors require external time-dependent (deterministic and/or stochastic) forces lacking the detailed balance symmetry and perpetually driving the system

out of equilibrium. Alternatively, the temperature can be either driven externally or kept position-dependent. In our case, no external driving or nonuniform temperature are necessary. The directed motion is entirely determined by the nonequilibrium system preparation, and it is not essential if the initial (nonequilibrium) kinetic energy $k_B T_{ne}/2$ is greater or smaller than the equilibrium kinetic energy, $k_B T_{eq}/2$. Second, with a few notable exceptions^{11,12,14,15,16,17,18,19,20,21,22,23,24,25}, the Brownian motors are normally studied in the overdamped limit. In any case, the inertia is not a key factor ensuring the directed motion of Brownian motors (although it is essential for the phenomenon of absolute negative mobility¹⁸ and sometimes is responsible for the very occurrence of the directed transport²²). On the contrary, our motor is operating in the inertial regime, and the effect is more pronounced in the gas phase, when friction $\xi \ll 1$ (Eq. (14)). The effect does not disappear in the overdamped limit, but becomes very small, $\langle v(t) \rangle \sim \xi^{-3}$ (Eq. (15)). This is entirely understandable, since the higher is the friction, the more rapidly $\rho_{ne}(v)$ relaxes to $\rho_B(v)$. However, if a reversible reaction $A \longleftrightarrow A'$ takes place in our ensemble, then $\rho_{ne}(v)$ can be recovered periodically. Third, the Brownian motors can be envisaged as been connected to two different heat baths.^{25,26,27} Similarly, the "blowtorch effect" (i.e. a nonuniform temperature profile along the potential surface, which, in the simplest case, can be realized within a two-bath model) can also induce a directed current.^{28,29} In our case, we can think of our motor as being connected to kinetic and potential baths, which are initially at different temperatures. In this sense, it can be treated as a molecular cycled Carnot engine.

Note that nonlinear dissipation effects can produce a directed motion of the Brownian particle provided its initial velocity distribution is asymmetric.³¹

The results presented in this work are not limited to a specific Gaussian form of the nonequilibrium distribution (3). Any distribution $\rho_{ne}(|v|)$ which differs from $\rho_B(v)$ gives rise to nonzero and periodic $\langle v(t) \rangle$. Realistic velocity distributions for dissociating molecules are described in papers.^{8,9,30} The theory can also be straightforwardly extended to rotational and vibrational motion.

Summarizing, we demonstrate that the gas of non-interacting particles trapped in an external asymmetric potential moves with nonzero oscillatory mean velocity $\langle v(t) \rangle$, provided its initial velocity distribution is produced at a temperature T_{ne} which differs from the equilibrium bath temperature, T_{eq} . The magnitude of the effect is determined by the value of $T_{ne} - T_{eq}$, and the direction of motion is determined by the sign of this expression. Practically, such a nonequilibrium distributions over molecular velocities and angular momenta are produced in the course of photodissociation,^{5,6,7,8,9} or due to any reaction of the kind $A \rightarrow A'$, provided it is rapid enough on the timescale of particle dynamics. In molecular dynamics simulations, we can instantaneously rescale molecular masses (that is equivalent to the rescaling of

temperature) and arrive at the nonequilibrium distribution (3). The phenomenon of occurrence of $\langle v(t) \rangle \neq 0$ is robust and does not require any careful tuning of the of the underlying parameters. It is not restricted to one-dimensional case and any asymmetric potential produces the effect, which will remain in the quantum case, too. Furthermore, our considerations do not contain any spe-

cific timescale and lengthscale, and are valid both for atomistic ensembles and for collections of macroscopic objects.

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